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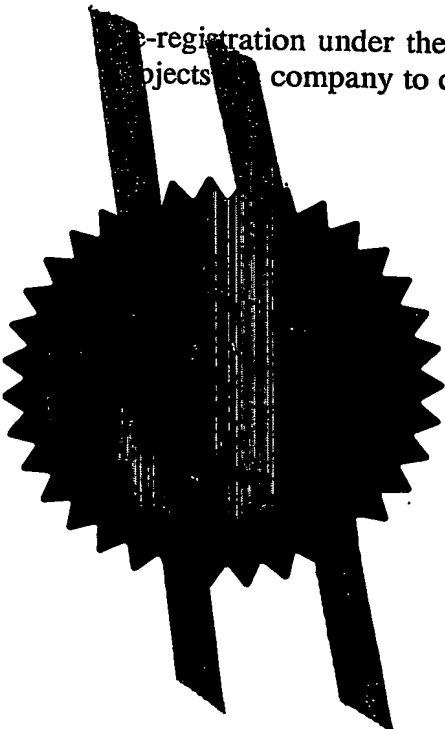
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Dated 18 March 2004



# Patents Form 1/77

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20 JUN 03 E816519-2 063844  
P01/77 0.00 0314368.2

## Request for grant of a patent

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THE PATENT OFFICE

20 JUN 2003

NEWPORT

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

SMC 60599/GB/P1

2. Patent application number

(The Patent Office will fill in this part)

20 JUN 2003

0314368.2

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Avecia Limited  
Hexagon House  
Blackley  
Manchester, M9 8ZS

Patents ADP number (if you know it)

07764137001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

Composition, Use and Process

5. Name of your agent (if you have one)

MAYALL, John

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Avecia Limited  
Hexagon House  
PO Box 42  
Blackley  
Manchester M9 8ZS

Patents ADP number (if you know it)

6244313002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
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Date of filing  
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or


c) any named applicant is a corporate body.

See note (d))

## Patents Form 1/77

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Continuation sheets of this form

	Description	14
	Claim(s)	3
	Abstract	1
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10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents  
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature G. Shepherd Date 19/6/03  
Avecia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

K.M.Pinder/G.Shepherd 0161 721 1361/2

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## COMPOSITION, USE AND PROCESS

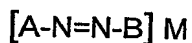
This invention relates to metal chelate compounds, to inks and to their use in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

WO 01/48090 relates to metal chelate compounds which comprise a naphthol component and certain heterocyclic groups. WO 01/48090 does not disclose such compounds substituted by a pyridyl ring attached to an azo group in the alpha position. Furthermore, WO 01/48090 does not disclose the fact that such substituted compounds have superior properties for use in ink jet printing applications.

According to the present invention there is provided a metal chelate compound of

Formula (1):

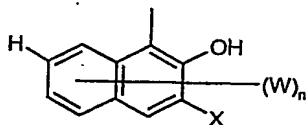


Formula (1)

wherein:

A is an optionally substituted pyridyl ring; and

B is of the Formula (2):



Formula (2)

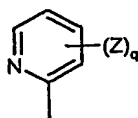
wherein:

X and W are substituents other than H;

M is a metal chelated to A-N=N-B; and

n is 0 to 4.

A is preferably of the Formula (3):



Formula (3)

wherein:

q is 0, 1, 2, 3 or 4; and

each Z independently is a substituent other than H.

5 Preferably each W, X and Z independently is CF<sub>3</sub>, -OH, -Br, -Cl, -F, -CN, -NO<sub>2</sub>, phosphoric acid, sulpho, optionally substituted phosphoramidate, optionally substituted alkyl, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted aralkyl, -SR<sup>1</sup>, -SO<sub>2</sub>R<sup>1</sup>, -SO<sub>2</sub>NR<sup>2</sup>R<sup>3</sup>, -SOR<sup>1</sup>, -OR<sup>1</sup>, -C(O)R<sup>1</sup>, -C(O)OR<sup>1</sup>, -C(O)NR<sup>2</sup>R<sup>3</sup>, -NR<sup>2</sup>R<sup>3</sup> or -NHCOR<sup>1</sup>, wherein  
10 R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently H, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl or optionally substituted aralkyl;

When W, X or Z is optionally substituted phosphoramidate it is preferably unsubstituted or substituted by optionally substituted alkyl, optionally substituted aryl or  
15 optionally substituted aralkyl. Preferred substituents include, for example, methyl, ethyl, n-propyl, iso-propyl, hydroxyethyl, optionally substituted phenyl or optionally substituted benzyl.

When W, X or Z is optionally substituted alkoxy it is preferably optionally substituted C<sub>1-6</sub>-alkoxy, optionally substituted by -Cl, -F, -Br, -CN, -OH or -CO<sub>2</sub>H. Most  
20 preferably Z is unsubstituted C<sub>1-6</sub>-alkoxy.

When W, X or Z is optionally substituted alkyl it is preferably optionally substituted C<sub>1-4</sub>-alkyl, more preferably C<sub>1-4</sub>-alkyl optionally substituted by halo, hydroxy, carboxy, sulpho or cyano. Examples include methyl, ethyl, n-propyl, iso-propyl, trifluoromethyl, hydroxyethyl, cyanoethyl, sulphopropyl and carboxyethyl. When Z is optionally  
25 substituted alkyl it is especially preferably methyl, ethyl or trifluoromethyl.

When W, X or Z is optionally substituted alkenyl, it is preferably optionally substituted C<sub>2</sub>-C<sub>4</sub> alkenyl.

When W, X or Z is optionally substituted alkynyl, it is preferably optionally substituted C<sub>2</sub>-C<sub>6</sub> alkynyl.

30 When W, X or Z is optionally substituted aryl, it is preferably optionally substituted phenyl, optionally substituted naphthyl or optionally substituted heteroaryl, especially optionally substituted phenyl or optionally substituted heteroaryl.

Preferred optional substituents on W, X or Z when W, X or Z is optionally substituted aryl are selected from sulpho, carboxy, nitro, cyano, halo (preferably chloro),  
35 alkoxy (preferably C<sub>1-6</sub>-alkoxy), alkyl (preferably C<sub>1-6</sub>-alkyl, optionally substituted by

halogen (preferably fluoro)), hydroxy, carboxy, phosphoric acid and sulpho. When W, X or Z is optionally substituted aryl it is especially substituted by C<sub>1-4</sub>-alkyl, carboxy, phosphoric acid, halogen (preferably fluoro), hydroxy and sulpho.

When W, X or Z is optionally substituted aralkyl, it is preferably optionally substituted benzyl.

Z is most preferably, -SH, carboxy, cyano, halo (preferably, bromo, chloro or fluoro), nitro, C<sub>1-6</sub>-alkoxy or C<sub>1-6</sub>-alkyl, optionally substituted by hydroxy, carboxy, halo (preferably fluoro) or cyano.

R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are preferably each independently H, optionally substituted C<sub>1-4</sub>-alkyl or optionally substituted aryl, more preferably H, C<sub>1-4</sub>-alkyl optionally substituted by hydroxy, carboxy, sulpho or cyano or phenyl optionally substituted by hydroxy, carboxy, sulpho, nitro, trifluoromethyl or cyano. Examples of groups represented by R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> include methyl, ethyl, n-propyl, iso-propyl, hydroxyethyl, cyanoethyl, sulphopropyl, carboxyethyl or carboxyphenyl. It is especially preferred that R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are H, optionally substituted C<sub>1-4</sub>-alkyl (for example, trifluoromethyl, hydroxyethyl or cyanoethyl), or optionally substituted aryl (for example phenyl optionally substituted by carboxy).

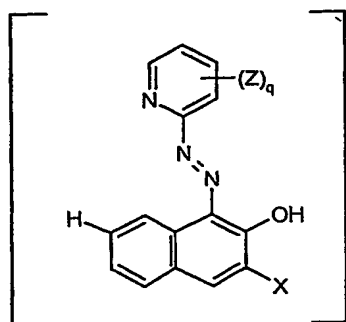
It is preferred that the pyridyl ring A is un-substituted or carries one or more substituents selected from -SH, carboxy, cyano, halo (preferably, bromo, chloro or fluoro), nitro, C<sub>1-6</sub>-alkoxy or C<sub>1-6</sub>-alkyl, optionally substituted by hydroxy, carboxy, halo (preferably fluoro) or cyano.

Preferably q is 0, 1, 2, 3 or 4, more preferably 0, 1 or 2.

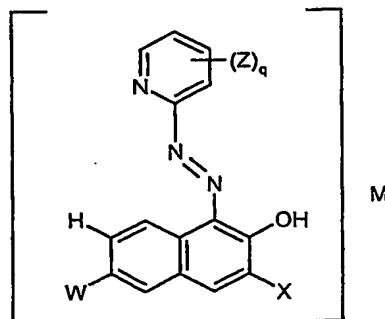
M preferably comprises one or more of the following metals: nickel, chromium, cobalt, copper, zinc, iron or manganese. It is particularly preferred that M is nickel or copper, most preferably Nickel. M is able to chelate to A-N=N-B in the ratio 1:1, 2:1, 2:2, 2:3 respectively and non-stoichiometric mixtures thereof. Preferably M is able to chelate to A-N=N-B in the ratio 1:1 or 2:1 respectively.

Preferably n is 0, 1, 2, 3 or 4, more preferably 1 or 2, especially 1.

Preferably the compound of Formula (1) is a metal chelate compound of Formula (4a) or (4b) or a salt thereof:



Formula (4a)



Formula (4b)

wherein:

M is nickel chelated to the group shown in square brackets; and

X and W are selected from sulpho, sulphonamido, carboxy, carbonamide, halogen, nitro and cyano groups;

5 q is 0, 1 or 2; and

Z is selected from cyano, C<sub>1-4</sub>-alkyl, carboxy, nitro, halo and C<sub>1-6</sub>-alkoxy groups.

It is especially preferred that the compounds of Formula (1) are magenta in colour that is, the compounds possess a  $\lambda$  max in the range 490-570nm.

10 The compounds of the invention exhibit particularly good ozone fastness, optical density and light fastness, making them valuable colorants for photorealistic and other ink jet printing applications.

The compounds of Formula (1) also have good solubility and operability in ink jet printers with a low tendency to crust over or block nozzles when inks containing the  
15 compounds are used in an ink jet printer.

Compounds of Formula (1) are preferably free from fibre reactive groups because no such groups are required. The term fibre reactive group is well known in the art and is described for example in EP 0356014 A1. Fibre reactive groups are capable, under suitable conditions, of reacting with the hydroxyl groups present in cellulosic fibres or with  
20 the amino groups present in natural fibres to form a covalent linkage between the fibre and the dye. As examples of fibre reactive groups which are preferably absent from the compounds of Formula (1) there may be mentioned aliphatic sulphonyl groups which contain a sulphate ester group in the beta-position to the sulphur atom, e.g. beta-sulphatoethylsulphonyl groups, alpha, beta-unsaturated acyl radicals of aliphatic carboxylic acids,  
25 for example acrylic acid, alpha-chloro-acrylic acid, alpha-bromoacrylic acid, propiolic acid, maleic acid and mono- and dichloro maleic; also the acyl radicals of acids which contain a substituent which reacts with cellulose in the presence of an alkali, e.g. the radical of a halogenated aliphatic acid such as chloroacetic acid, beta-chloro and beta-bromopropionic acids and alpha, beta-dichloro- and dibromopropionic acids or radicals of  
30 vinylsulphonyl- or beta-chloroethylsulphonyl- or beta-sulphatoethylsulphonyl-endo-methylene cyclohexane carboxylic acids. Other examples of cellulose reactive groups are tetrafluorocyclobutyl carbonyl, trifluoro-cyclobutenyl carbonyl, tetrafluorocyclobutylethenyl carbonyl, trifluoro-cyclobutenylethenyl carbonyl; activated halogenated 1,3-dicyanobenzene radicals; and heterocyclic radicals which contain 1, 2 or 3 nitrogen atoms  
35 in the heterocyclic ring and at least one cellulose reactive substituent on a carbon atom of the ring.

The compounds described herein may exist in tautomeric forms other than those shown in this specification. These tautomers are also included within the scope of the present inventions.

The compounds of Formula (1) may be in the free acid or salt form. Preferred salts are water-soluble, for example alkali metal salts, (especially lithium, sodium, potassium); ammonium, substituted ammonium and mixed salts thereof. Preferred metal salts are those with sodium, lithium, ammonium and substituted alkyl ammonium salts.

5 Preferred ammonium and substituted alkyl ammonium salts have cations of the formula  $^+NV_4$  wherein each V independently is H or optionally substituted alkyl, or two groups represented by V are H or optionally substituted alkyl and the remaining two groups represented by V, together with the N atom to which they are attached, form a 5- or 6- membered ring (preferably a morpholinyl, pyridinyl or piperidinyl ring).

10 Preferably each V independently is H or  $C_{1-4}$ -alkyl, more preferably H,  $CH_3$  or  $CH_2CH_3$ , especially H.

Examples of cations include  $^+NH_4$ , morpholinium, piperidinium, pyridinium,  $(CH_3)_3N^+H$ ,  $(CH_3)_2N^+H_2$ ,  $H_2N^+(CH_3)(CH_2CH_3)$ ,  $CH_3N^+H_3$ ,  $CH_3CH_2N^+H_3$ ,  $H_2N^+(CH_2CH_3)_2$ ,  $CH_3CH_2CH_2N^+H_3$ ,  $(CH_3)_2CHN^+H_3$ ,  $N^+(CH_3)_4$ ,  $N^+(CH_2CH_3)_4$ , N-methyl pyridinium, N,N-dimethyl piperidinium and N,N-dimethyl morpholinium.

15 It is especially preferred that the compound of Formula (1) is in the form of a sodium, lithium, potassium, ammonium or substituted ammonium salt, because we have found that these salts provide prints which exhibit a high light-fastness when incorporated into an ink jet printing ink.

20 The compounds of Formula (1) may be converted into a salt using known techniques. For example, an alkali metal salt of a compound may be converted into a salt with ammonia or an amine by dissolving an alkali metal salt of the dye in water and passing the solution through a column of a suitably modified ion exchange resin.

25 The compounds of Formula (1) may be prepared using conventional techniques for the preparation of metal chelate compounds and non-stoichiometric mixtures thereof. For example, a suitable method comprises mixing together a metal salt and a compound of Formula  $A-N=N-B$  in solution, wherein A and B are as hereinbefore defined.

30 The product of the above process may be converted to a salt by conventional techniques as hereinbefore described. Alternatively, the product may be isolated in its free acid form by acidifying the reaction mixture, preferably using a mineral acid, for example hydrochloric acid and when the product precipitates as a solid it may be separated from the mixture by filtration. Unwanted anions may be and preferably are removed from the product of the above process by dialysis, osmosis, ultra filtration or a combination thereof. Alternatively, the product solution is subjected to the above purification directly without isolation of the product.

35 The compounds of Formula  $A-N=N-B$  may be prepared by, for example, diazotising the N-oxide of amino-pyridine  $A-NH_2$  to give a diazonium salt and coupling the resultant diazonium salt with a compound of the Formula  $H-B$ , wherein A and B are as hereinbefore defined. The diazotisation is preferably performed at a temperature below



20°C, more preferably at a temperature in the range -0°C to 5°C. Preferably the diazotisation is performed in dilute acid, preferably at a pH below 7. Dilute mineral acid, e.g. HCl or H<sub>2</sub>SO<sub>4</sub> or an organic acid for example acetic acid, phosphoric acid or a mixture thereof are often used to achieve the desired acidic conditions. The N-oxide can then be  
5 cleaved to provide the compound of Formula A-N=N-B.

Alternatively, the compounds of Formula (1) can be prepared by diazotising a compound of formula A-NH<sub>2</sub> to give a diazonium salt e.g. using sodium ethoxide and iso-amyl nitrite, followed by coupling the diazonium salt onto a compound of formula H-B to provide a compound of Formula A-N=N-B.

10 Compounds of Formula A-N=N-B can then be converted to the corresponding metal complexes [A-N=N-B]M by treatment with metal salts, such as for example nickel (II) chloride or nickel (II) acetate.

The present invention also provides mixtures comprising two or more compounds of the Formula (1) or salts thereof. Furthermore, the compounds of Formula (1) may be  
15 mixed with commercially available dyes, especially those listed in the Colour Index International, to adjust the shade or other properties as desired.

According to a second aspect of the present invention there is provided a composition comprising:

- (a) one or more compound according to the first aspect of the present  
20 invention; and
- (b) one or more water-soluble dye other than a compound according to the first aspect of the invention.

The other water-soluble dye is preferably a water-soluble magenta dye, for example a xanthene dye, an azo or bis azo dye.

25 Preferred other water-soluble magenta dyes include C.I. Acid Red 50, 52, 87, 91, 92, 95, 249 and 289; CI Direct Red 252; pacified Reactive Red 23; C.I. Direct Violet 106 and 107; compounds 100 to 107, 200 and 201 described on pages 8 and 9 of WO96/24636; compounds 1 to 24 shown described on columns 4 to 10 in US 5,542,970; compounds 1 to 55 described on pages 7 to 17 of EP-A-682 088; compounds 1 to 14  
30 shown in Example 1 to 6 of EP-A-194,885; compounds 1 to 24 described on pages 8 to 13 of EP-A-717 089; the compounds described in examples 1 to 16 in columns. 5 to 11 of US 5,262,527; and the dyes described in Examples 1 to 21 in WO 94/16021.

The composition according to the second aspect of the present invention preferably comprises from 1 to 99, more preferably from 3 to 70 and especially from 5 to  
35 50 parts in total of Component (a); and from 99 to 1, more preferably from 30 to 97 parts and especially 95 to 50 parts in total of Component (b), wherein the parts are by weight and the sum of the parts (a) + (b) = 100.

The composition may contain a single dye of Formula (1) or a mixture thereof. Similarly, the composition may contain a single water-soluble magenta dye or a mixture of two or more water-soluble magenta dyes.

5 The compounds and compositions according to the first and second aspects of the present invention may be, and preferably are, purified to remove undesirable impurities before they are incorporated into inks for ink jet printing. Conventional techniques may be employed for purification, for example ultrafiltration, reverse osmosis and/or dialysis.

According to a third aspect of the present invention there is provided an ink comprising:

- 10 (i) a compound according to the first aspect of the present invention, or a composition according to the second aspect of the invention; and  
(ii) a liquid medium.

The liquid medium preferably comprises: water; a mixture of water and an organic solvent; or an organic solvent free from water.

15 The number of parts by weight of component (i) of the ink is preferably from 0.01 to 30, more preferably 0.1 to 20, especially from 0.5 to 15, and more especially from 1 to 5 parts. The number of parts by weight of component (ii) is preferably from 99.99 to 70, more preferably from 99.9 to 80, especially from 99.5 to 85, and more especially from 99 to 95 parts. The number of parts (i) + (ii) is 100 and all parts mentioned here are by weight.

20 Preferably component (i) is completely dissolved in component (ii). Preferably component (i) has a solubility in component (ii) at 20°C of at least 10%. This allows the preparation of concentrates which may be used to prepare more dilute inks and reduces the chance of the compound(s) of component (i) of the ink precipitating if evaporation of the liquid medium occurs during storage.

25 When the liquid medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred  
30 water-miscible organic solvents include C<sub>1-6</sub>-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene  
35 glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C<sub>1-4</sub>-alkyl ethers of diols, preferably mono-C<sub>1-4</sub>-alkyl ethers of diols

having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy] ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulfoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably  $\text{CH}_2\text{Cl}_2$ ; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include  $\text{C}_{1-4}$ -alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and/or an alcohol (especially a  $\text{C}_{1-4}$ -alkanol, such as ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Inks comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

Preferred low melting solid media have a melting point in the range from 60°C to 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with  $\text{C}_{18-24}$  chains, and sulphonamides. A compound of Formula (1) may be dissolved in the low melting point solid or may be finely dispersed in it.

The inks according to the present invention may of course also contain further additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives, anti-cockle agents to reduce paper curling and surfactants which may be ionic or non-ionic.

The pH of the ink is preferably from 4 to 11, more preferably from 7 to 10.

The viscosity of the ink at 25°C is preferably less than 50cP, more preferably less than 20cP and especially less than 5cP.

When the inks according to the invention are used as ink jet printing inks, the ink preferably has a concentration of less than 500 parts per million, more preferably less than 100 parts per million of halide ions. It is especially preferred that the ink has less than 100, more preferably less than 50 parts per million of divalent and trivalent metals, wherein parts refer to parts by weight relative to the total weight of the ink. We have found that purifying the inks to reduce the concentration of these undesirable ions reduces nozzle blockage in ink jet printing heads, particularly in thermal ink jet printers.

The inks of the present invention preferably form the magenta ink of a standard magenta, yellow, cyan and black ink set. Typically in such an ink set the yellow ink will contain CI Direct yellow 86, 142 or Pro-Jet™ Fast yellow 2; the cyan ink will contain CI Direct blue 86, 199 or Pro-Jet™ Fast cyan 2; and the black ink will contain CI Direct black 199 or Pro-Jet™ Fast black 2 (Pro-Jet is a trademark of Avecia Limited).

A fourth aspect of the present invention provides a process for printing an image on a substrate comprising applying thereto by means of an ink jet printer an ink containing a compound according to the first aspect of the invention or a composition according to the second aspect of the invention. The ink used in this process is preferably as defined in the third aspect of the present invention.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc.), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper, Xerox Acid Paper (available from Xerox).

A fifth aspect of the present invention provides a substrate, preferably a paper, an overhead projector slide or a textile material, printed with an ink according to the third aspect of the present invention or by means of the process according to the fourth aspect of the present invention.

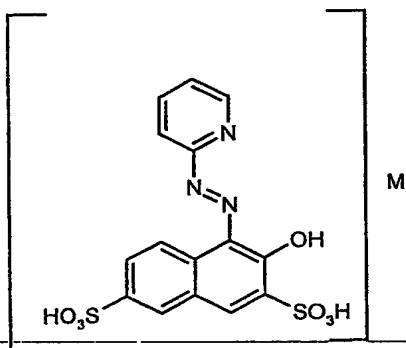
According to a sixth aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and ink, wherein the ink is present in the chamber and the ink contains a compound or a composition according to the first or second aspect of the present invention. Preferably the ink is as defined in the third aspect of the present invention.

According to a seventh aspect of the present invention there is provided an ink jet printer containing an ink jet printer cartridge, wherein the ink jet printer cartridge is as defined in the sixth aspect of the present invention.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

#### Example 1

##### Preparation of Compound (1) wherein M is nickel



Compound (1)

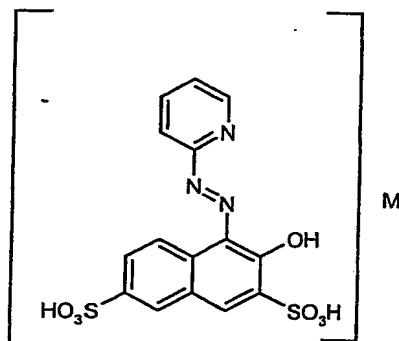
Compound 1 was prepared according to the stages (a) and (b):

##### Stage (a): Preparation of 2-hydroxy-1-[pyridin-2-yl diazenyl]naphthalene-3,6-disulfonic acid

2-hydroxy-1-[pyridin-2-yl diazenyl]naphthalene (20g, 0.08mol) was added over 30 minutes to ice cold fuming sulphuric acid (20% sulphur trioxide, 150ml). Once the addition was complete the reaction temperature was slowly raised to 60°C and held at that temperature for 1.5 hours. The mixture was allowed to cool before being added to ice (1kg) to give an orange suspension. The solid was collected by filtration, washed with sodium chloride solution and acetone to give 57g of an orange solid (91% yield, 52% purity). Analysis by mass spectrometry found : M/Z 204 (100% (M-2H)<sup>2+</sup>); 408 (45% (M-H)<sup>+</sup>).

Stage (b): Preparation Compound (1)

The product from stage (a) (5g, 6.4mmol) was dissolved in water at pH = 6 (150ml). An aqueous solution of nickel chloride hexahydrate (8.5ml of a 0.4mol dm<sup>-3</sup> solution) was added dropwise causing the colour to become deeper and the pH to fall. The pH was restored to pH 6-7 and the reaction mixture stirred at 70-80°C for 2 hours. After cooling the dye was precipitated by the addition of sodium chloride and collected by filtration. The dye was reconstituted and dialysed to low conductivity through a dialysis membrane, to give 1g of solid.  $\lambda_{\max}(\text{water})$  523, 562nm.

Example 2Preparation of Compound (2) wherein M is nickel

Example 2 was prepared by following the same procedure as described for compound (1) of example 1, with the exception that in stage (b) 17.5ml of a 0.4mol dm<sup>-3</sup> nickel chloride solution was used. 2.1g of solid was collected  $\lambda_{\max}(\text{water})$  518, 555nm.

Inks

The inks described in Tables I and II may be prepared wherein the Compound described in the first column is the Compound made in the above Examples of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in Table I and II:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

5

BDL = butane-2,3-diol

CET = cetyl ammonium bromide

PHO =  $\text{Na}_2\text{HPO}_4$  and

TBT = tertiary butanol

TDG = thiodiglycol

10

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TABLE I

Dye	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
2	10.0	85	3		3	3				5	1	
1	2.1*	91		8								1
1	3.1	86	5				0.2	4				5
1	1.1	81			9		0.5				9	
2	2.5	60	4	15	3	3		6	10	10	5	4
1	5	65		20				10				
1	2.4	75	5	4		5				6		5
2	4.1	80	3	5	2	10	0.3					
2	3.2	65		5	4	6			5	4	6	5
1	5.1	96								4		
2	10.8	90	5						5			
1	10.0	80	2	6	2	5			1		4	
2	1.8	80		5							15	
2	2.6	84			11						5	
1	3.3	80	2			10				2		6
1	12.0	90				7	0.3		3			
2	5.4	69	2	20	2	1					3	3
2	6.0	91			4						5	



TABLE II

Dye	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2				1.2	5	5
2	9.0	90		5								
2	1.5	85	5	5		0.15	5.0	0.2		0.12		
2	2.5	90		6	4							6
1	3.1	82	4	8		0.3			5	0.2		
1	0.9	85		10								
2	8.0	90		5	5			0.3				11
2	4.0	70		10	4				1		4	
1	2.2	75	4	10	3				2		6	
2	10.0	91			6						3	
1	9.0	76		9	7		3.0			0.95	5	
1	5.0	78	5	11							6	
2	5.4	86			7						7	
2	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5	
1	2.0	90		10								
1	2	88						10				
2	5	78			5			12			5	
1	8	70	2		8			15			5	
1	10	80						8			12	
1	10	80		10								

CLAIMS

1. A metal chelate compound of Formula (1) or a salt thereof:

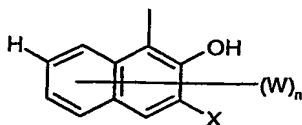


Formula (1)

wherein:

A is an optionally substituted pyridyl ring; and

10 B is of the Formula (2):



Formula (2)

wherein:

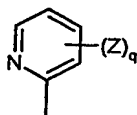
X and W are substituents other than H;

M is a metal chelated to A-N=N-B; and

15 n is 0 to 4.

2. A compound according to claim 1 wherein :

A is of the Formula (3):



Formula (3)

20

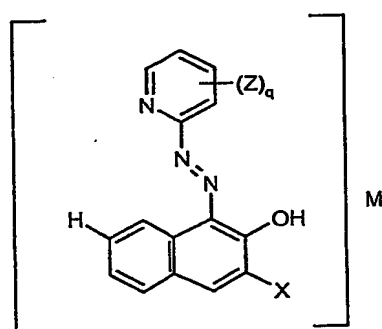
q is 0, 1, 2, 3 or 4; and

each Z independently is a substituent other than H.

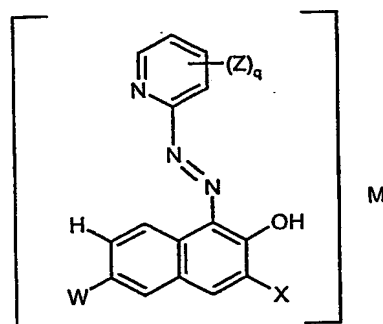
3. A compound according to claim 1 or 2 wherein X, W and Z are each independently  
 25 selected from -OH, -Br, -Cl, -F, -CF<sub>3</sub>, -CN, -NO<sub>2</sub>, phosphoric acid, sulpho, optionally substituted phosphoramidate, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted aralkyl, -SR<sup>1</sup>, -SO<sub>2</sub>R<sup>1</sup>, -SO<sub>2</sub>NR<sup>2</sup>R<sup>3</sup>, -SOR<sup>1</sup>, -OR<sup>1</sup>, -C(O)R<sup>1</sup>, -C(O)OR<sup>1</sup>, -C(O)NR<sup>2</sup>R<sup>3</sup>, -NR<sup>2</sup>R<sup>3</sup> and -NHCOR<sup>1</sup>, wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are as described in claim 2.

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4. A compound according to any one of the preceding claims wherein Z is selected from -SH, carboxy, cyano, halo (bromo, chloro, fluoro), nitro, C<sub>1-6</sub>-alkoxy or C<sub>1-6</sub>-alkyl, optionally substituted by hydroxy, carboxy, halo (preferably fluoro) or cyano group.
5. A compound according to any one of the preceding claims wherein X and W are each selected from sulpho, sulphonamido, carboxy, carbonamide, halogen, nitro and cyano groups.
6. A compound according to any one of the preceding claims wherein M is nickel, chromium, cobalt, copper, zinc, iron or manganese.
7. A compound according to any of the preceding claims wherein M is copper or nickel.
8. A compound according to any one of the preceding claims of Formula (4a) or (4b):



Formula (4a)



Formula (4b)

wherein:

M

is nickel, chelated to the group shown in square brackets; and

20

X and W

are selected from sulpho, sulphonamido, carboxy, carbonamide, halogen, nitro and cyano groups;

q

is 0, 1 or 2; and

Z

is selected from cyano, C<sub>1-4</sub>-alkyl, carboxy, nitro, halo and C<sub>1-6</sub>-alkoxy groups.

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9.

A composition comprising:

(a) one or more compound according to any one of the preceding claims; and

(b) one or more water-soluble dye other than a compound according to any one of the preceding claims.

30

10. An ink comprising:

- (a) a compound according to any one of claims 1 to 8, or a composition according to claim 9; and
- (b) a liquid medium.

5

11. A process for printing an image on a substrate comprising applying thereto by means of an ink jet printer an ink according to claim 10.

10

12. A substrate printed with an ink according to claim 10 or by means of the process according to claim 11.

13. An ink jet printer cartridge comprising a chamber and ink, wherein the ink is present in the chamber and the ink is as defined in claim 10.

15 14. An ink jet printer containing an ink jet printer cartridge, wherein the ink jet printer cartridge is as defined in claim 13.

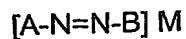
15. A compound according to claim 1 substantially as herein described with reference to any one of the examples.

20

16. An ink according to claim 10 substantially as herein described with reference to any one of the examples.

ABSTRACTCOMPOSITION, USE AND PROCESS

5 A metal chelate compound of Formula (1) or a salt thereof:

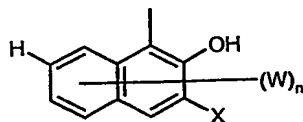


Formula (1)

10 wherein:

A is an optionally substituted pyridyl ring; and

B is of the Formula (2):



Formula (2)

wherein:

15 X and W are substituents other than H;

M is a metal chelated to A-N=N-B; and

n is 0 to 4,

also claimed are compositions and inks containing a compound of Formula (1), a process for ink jet printing using the inks and an ink jet printer cartridge containing the ink.

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